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ORGANIC NONLINEAR OPTICAL MATERIALS

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Translation of "Yuuki Hisenkei Koogaku Zairyoo", Oyo Butsuri 1985, 54 (2), 137-42

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16. Abstract

A review on the title organic compounds, e.g., urea, $O_2NC_6H_4NH_2$, I, II, etc., with 50 references.

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ORGANIC NONLINEAR OPTICAL MATERIALS

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(accepted on Oct. 12 1984)

Recently, it has been becoming clear that organic compounds with delocalized π electrons show a great nonlinear optical response. Especially, secondary nonlinear optical constants of more than 2 digits have often been seen in the molecular level compared to the existing inorganic crystals such as $LiNbO_3$. The crystallization has been continuously tried. Organic nonlinear optical crystals have a new future as new materials for use in the applied physics such as photomodulation, optical frequency transformation, opto-bi stabilization, and phase conjugation optics.

1. Introduction.

We would like to look at the present situation of organic nonlinear optical materials by glancing back at their history. The optical nonlinear response of organic compound was first paid attention to way back in 1964 by Rentzepis 1) and Heilmeyer 2). They observed optical secondary higher harmonic generation (SHG) of ruby laser and Nd:YAG laser using 3,4 benzopyrene, 1,2

benzanthracene and hexamine. Rentzepis used the material which has a benzen ring which is the constitutional element of organic nonlinear optical crystals. Heilmeyer has confirmed that secondary nonlinear optical constants which contribute to SHG, and primary electro optical coefficients are about the same in a sensitivity comparison. In other words, it is the delocalized π electron and the electronic polarization which is not affected by such as lattice vibrations that mainly contributes to the nonlinear polarization of organic compounds. For the former SHG obsevation, polycrystal powder was used as a specimen. But Kurtz and others 3) analyzed the simple method to estimate the secondary nonlinear optical constant, and used it to find both the organic and non-organic nonlinear optical materials. Among the materials which were estimated to have a large nonlinear optical constant, are $LiIO_3$ as a non-organic compound, which has less optical damage and is often used as SHG and Urea, m-dinitrobenzen as an organic compound. This powder method 4) was a clue to a organic compounds search, and 5-nitrouracil (5-NU) 5), m-nitroaniline (m-NA) which are organic compounds carrying the same constant as $LiIO_3$ 5) are found and are studied regarding their crystalizatons. The SHG observation method which organizes the orientation of molecules in a gas by electrostatic field was applied to organic molecules in a liquid 6)

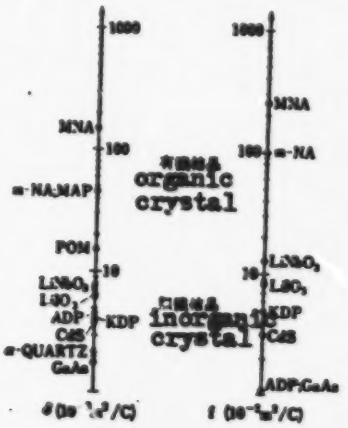

Fig. 1 Index of merit of scondary nonlineal opt. constant and primary electro opt. coeff., , f are compared on organic and inorganic crystals

(From Laser Focus)

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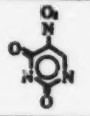
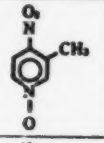
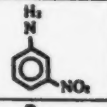
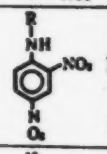
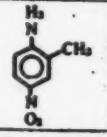
TABLE 1 CHARACTERISTICS OF ORGANIC NONLINEAR OPTICAL CRYSTALS

name	structure	symmetry	d_{ijk}($\times 10^{-12}$ m/V)	r_{ijk}**($\times 10^{-12}$ m/V)	reference
UREA		42m Tetragonal system	$d_{36}=1.7$	$r_{14}=5.6$ $r_{36}=2.5$	20)
5-NU		$P2_12_12_1$ Rhombic sys.	$d_{14}=d_{25}=d_{36}=5.0$	—	5)
POM		$P2_12_12_1$ Rhombic sys.	$d_{14}=d_{25}=d_{36}=8.0$	$r_{14}=3.6$ $r_{25}=5.1$ $r_{36}=2.6$	14)
m-NA		$P_{na}2_1$ Rhombic sis.	$d_{31}=15.6$ $d_{32}=1.2$ $d_{33}=16.4$	$r_{31}=7.4$ $r_{33}=16.7$	21)
MAP		$P2_1$ Monoclinic sis.	$d_{21}=16.6$ $d_{22}=17.6$ $d_{23}=3.5$	—	15)
MNA		$P2_1$ Monoclinic sis.	$d_{11}=250.0$ $d_{12}=30.0$	$r_{11}=67.0$	10) 11)

*) R: (CH_3)-CH-(CO_2CH_3)

**) r is a value for the wave of 0.633um

by Levine and others 7) in 1974. And by the Maker Fringe method 8) the polarizability of the primary molecules and ultramicro polarizability. This dcSHG method 9) was extremly effective and useful for measuring the nonlinear optical constant in molecule level. It was a method to pursue the theoretical origins of the nonlineal polarization that is typical to organic compunds, and advanced the systemat research of the new organic nonlinear optical materials.

It was became clear theoretically and experimentaly that when a donor and a accepter are given to a benzen, the π electron system as substituents, nonlinear character grows due to the charge transfer effect. Levine and others 10) pointed out in 1979, that the MNA (methylnitroaniline) crystal in which NH_2, CH_3 as donor

and NO_2 as accepter are configurated to a benzen ring, has a large secondary nonlinear optical constant. Thereafter, the organic nonlinear optical crystal became popular to research. In 1981, Garito and others 11) confirmed that the primary electro optical coeff. is also as large as the secondary nonlinear optical constant. In 1982, at the symposium by the U.S. Chemical Society, general reports of the research on organic nonlinear optical materials are presented mainly from the U.S. and France 12). In these couple of years, the organic nonlinear optical materials have been getting some attention. We will mention here the secondary nonlinear properties, crystalized compounds, their theory, evaluation, and their future.

2. Organic Nonlinear Optical Single Crystals.

Fig.1 shows the comparison of derivatives, semiconductors and organic crystals between the secondary nonlinear optical constant and the primary electro optical coeff., δ, f 13). is an amount called the Delta of Miller. It is expressed as $\delta = d / \varepsilon_0 \chi^{(1)}(\omega)^2 \chi^{(2)}(2\omega)$ where d is the secondary nonlinear optical constant for SHG is d and the linear susceptability in the basic wave and the secondary high harmonic of the angular frequency w are $\chi^{(1)}(\omega), \chi^{(2)}(2\omega)$. ε_0 is permittivity in a vaccumed condition. f is expressed as $f = r/\varepsilon(\varepsilon - 1)$ where r is the primary electro optical coeff., ε is permittivity. The generating efficiency of SHG is relative to δ^2, so MNA has about a 2000 times larger efficiency than $LiNbO_3$. Semiconducter materials such as GaAs have large nonlinear optical constants but δ becomes small after all since the refractive index is large. However, organic crystals have small refractive indexes in visible

infrared wave areas. Fig. 1 shows clearly that organic crystals have a far larger index of merit compared to inorganic crystals. POM stands for 3-methyl-4-nitropyridine-1-oxide 14), MAP stands for 3-methyl-(2-4-dinitrophenyl)-aminopropanoate 15).

Crystals large enough to be actually used now are few such as UREA 16,17) m-NA with a relatively small index of merit. Table 1 show the secondary nonlinear optical constant d_{ijk} , primary erectro optical coeff. r_{ijk} , organic nonlinear optical crystals in which permittivity and its dispersion is measured. Each constant of nonlinear optical crystals is noted in reference 18,19). 1138

For the growth of crystals listed in Table 1, except for the chemical vapor deposition which is used in MNA, the method of solvent vapor deposition from saturable solution is used.

3. Molecular Polarizability

3.1 Evaluation method for secondary nonlinear optical constants.

3.1.1 Powder method

Secondary nonlinear optical constants of a copound in a multicrystal condition can be evaluated by observing SHG scattered from a sample thinly lined on a glass plate. Kurtz and others 3) made equations to obtain the constant values through powder sizes and coherence lengths.

3.1.2 dcSHG method

dcSHG method is used for finding out the molecular polarizability and hyperpolarizability of organic compound which shows a secondary nonlinear reaction as a molecule but in which a

microscopic nonlinear optical constant becomes 0 due to its reversal symmetry when crysterized, or in which crysterization is difficult. In this method, SHG is observed by applying the electrostatic field from top and bottom of pallarel or wedge type cell, and organizing the orientation of the molecules. The light path and length in the parallel type cell is changed by turning the cell and in the wedge type cell is by moving the position of incidence to obtain Maker fringe. The molecular polarizability is estimated from the shape of the fringe. The coherenth length is obtained from the interval length.

Molecular polarizability p for the inner and outer electric field under dipole is expressed in (1)

$$p=\mu+\alpha E+\beta E^2+\gamma E^3+\cdots \qquad (1)$$

$\mu, \alpha, \beta, \gamma$ denote static diopole moment at molecule level, linear susceptibility, secondary and tertiary molecular polarizability. α, β, γ are the second, third, and forth step tensors respectively. When ab electrostatic field Eo is applied and a light wave of angular freq. w, amplitude Ew is emmited, the microscopic polarizability $P_{2\omega}$ in the solution is:

$$P_{2\omega}=\Gamma\varepsilon_0 E_\omega^2=d_{eff}E_\omega^2 \qquad (2)$$

$$\Gamma=N\gamma f_\omega f_\omega^2 f_{2\omega} \qquad (3)$$

$$\gamma=\gamma_0+\mu\beta/5kT \qquad (4)$$

where d_{eff} is nonlinear optical constant 6,7,22). In Equ.(3), N is the number of molecules in unit volume, is the correction of local field for the molecules in the solution with the electric field of angular freq. indicated in suffix. In Equ. (4), γ_0 is the term which contrubutes the tertial electro polarizability at pure

molecule level, the second term is considering the orientation of dipole against an electrostatic field. Since $\gamma \cdot \langle \mu\beta/kT$, secondary molecular polarization β can be obtained by dcSHG method. Of course the tertial nonlinear property for the molecules which do not have secondary nonlinear property at molecule level can be evaluated 22).

3.2 Source of nonlinear property in organic molecules.

σ-bonding at C-C, C-H which form the frame of organic molecules is not easily infulenced from the outer field. So it is the delocalized π electron that contributes to the nonlinear polarization. The conjugate π electron system often has reverse symmetry. By giving a substituent, it loses its symmetry, showing the secondary nonlinear property. The addition of substituent strains the conjugate π electron system, causes the forming of an unbalanced electron which is called the electromeric effect. Among those substituents, the one in which the mesomeric effect influences the delocalized π electron and which gives off an electron, is called the donor; the one which attracts the electron is called the accepter. Let's consider the case where the popular research object, the benzen ring is given a substituent. Benzen is of reverse symmetry in shape. The molecular polarization for the electric field E is:

$$p = a \cdot E + \gamma \cdot E^3 + \cdots \quad (E \text{ の奇数次の項のみ}) \quad (5)$$

(E with terms of odd number degrees)

The diopole (mesomeric moment) μ^{α} made by the strain of electron system because of the substituent is replaced as $M^2 \propto a \cdot E_i$

in the effective inner electric field E_i'. Putting $E_T = E_i + E$ instead of E in Equ. (5):

$$p = a.E_i + 3\gamma.E_i E^2 + \gamma.E^3 \quad \text{(6)}$$

From Equ. (1) and (6), $\mu = a.E_i$, $\beta = 3\gamma.E_i$, and the secondary nonlinear property is created 23,24). However, the diopole produced by the inductive effect of a substituent which strains σ bonding, greatly contributes to the permanent diopole μ in Equ. (1).

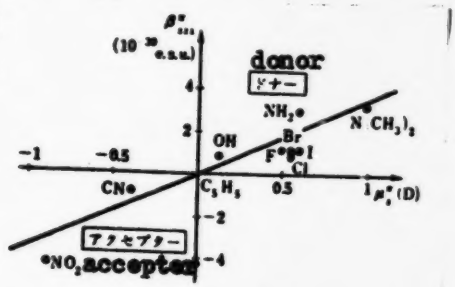


Fig. 2 Relations between Mesomeric moment and and secondary molecular polarizability.

β in $\beta \simeq \mu^2 \gamma / kT$ is for a molecule. If multiple numbers of molecules orient at random in a solution, microscopic secondary nonlinear polarizability becomes 0. When the electro static field E_0 is applied the orientation trys to organize under the heat vibrations. If $E = E_0 + E_\omega$ in Equ. (6), microscopic polarization of Equ. (2) is obtained from the second and the third term. The second term of Equ. (4), is obtained considering the Portsman distribution of the heat vibrations. The first term of Equ. (4) is from the third term of Equ. (6). Fig. 2 shows the mesurement of β aganst the mesomeric moment μ by a substituent 12). Both the horizontal and vertical axis β, μ have suffix x. This is becausethe polarization of the applied electric field // polarization of incident light wave in the dcSHG experiment is taken into account. 1139

The effect of a substituent has also been studied on pyridine and others 25). A substituent helps it to loose its reverse symmetry and the secondary nonlinear property appears, 1;and thus

it creates a much larger molecular polarizability than an inorganic compund due to the effect of organic molecules. By giving an accepter and a donor to the benzen ring, there is more effect than a simple added effect. This is because there is a charge transfer from a donor to an accepter through the benzen ring. Levine 26), Ouder 27) and others compared the secondary nonlinear molecular polarizabilities amoung o-, m-, and p-nitroaniline and found out that delocalization of π electron enlarges because of the charge transfer between the donor, so the accepter and secondary molecular polarizability grows. p-NA in which the position of the double bond changes and π electron easily moves, has 5 times bigger molecular polarizability β than m-NA in which π electron does not move easily. However the p-NA crystal has reverse symmetry. They also studied how a microscopic secondary nonlinear optical constant is made from molecular polarizability in a crystal 15,27). Another donor methyl group is added to to p-NA to make MNA.

It was around this time when the study of molecular 1140
polarizability using the quantum theory was started. The molecular orbitary theory 28), which is often used in recording various phenomena of benzen π electron group in the field of quantum chemistry, was used to calculate the secondary and tertialy molecular polarization, which agreed very well with the experiments 29,30). This theory was used on a quinonoid group, and it was found to have the secondary nonlinear polarization which is one digit larger than p-NA. These days, dispersion of the molecular polarization is also studied in detail 32), thus the molecular orbital method has been the theoretical method of the

molecule designing.

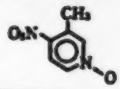
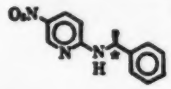
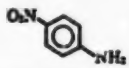
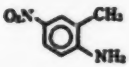
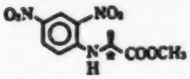
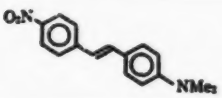
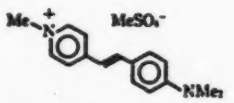
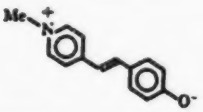
When only the ground states and the excited states of a molecular orbit are considered, the secondary molecular polarizability from the perturpation theory is:

$$\beta = 3\mu_{ge}^2(\mu_e - \mu_g)/2E^2 \qquad (7)$$

Here, μ_{ge}, μ_e, μ_g are each a transition dipole from the ground to excited state, permanent diople in excited state, permanent diople in ground state. E is the energy difference between the two states. Equ. (7) is expressed with two kind of linear bond of two molecular orbits, which are molecular orbits of ground and excited states, with a substituent creating a complete charge transfer, and without a substituent. It is effective in the transparent area where the dependability of wavelength can be ignored 25). When the delocalization of π electron gets larger, the charge transfer μ_{ge} get larger, the diffence of the ground and the excited states gets smaller, E gets smaller, β gets larger. Therefore, it can be said that the longer the conjugate chain of electron, the larger the secondary molecular polarizability. Table 2 shows the measured values d_{eff}, β for various organic conpounds using the powder and dcSHG methods, the limit of the transparent area in the short wave end corresponding to E. d_{eff} is a relative value with UREA = 1.

From Table 2, increase of β and the shift of cut-off waves to the long waves side can be seen. Besides the compounds listed in Table 2, there are many more compounds which have larger molecular polarizability than MNA, that are found; for example, DAN, PAN, PNP, MNNA 12). These throw some light on the organic nonlinear optical crystals as a new material.

TABLE 2 SECONDARY NONLINEAR OPTICAL CONSTANT OF ORGANIC CONSTANTS

Molecular const. (name)	d_{11}	$\beta(\times 10^{-30}$esu)	Cut-off wave (nm)
(UREA)	1	0.45	200
 (POM)	13	5	410
 (MBA-NP)	25	—	430
 (p-NA)	0.0	35	470
 (MNA)	22	42	480
 (MAP)	10	220	500
	0.0	450	430~580
	~250	—	473~588
	0.0	1000	570~650

Note: Me is methyl group. ~ in cut-off wave means solvent dependability.

4. Future development.

There are many problems for organic single crystals to be utilized for nonlinear optical purposes. A large crystal has to be made, to begin with. It depends on whether or not a large crystal can be made by controlling the orientation. There have been some experiments of solving this problem by polymerization which does not have an optical stability nor mechanical strength. SHG was observed by giving the MNA to its side chain 37). There have been also several polymerization studies on tertial nonlinear properties 18,30,38-40), and such as PTS (p-toluene-sulphonate) with higher index of merit than Ge, and GaAs was found. A large tertial nonlinear property can be used in optical phase conjugation 41). It is an electronic polarization so is expected as the fastest reactive intrinsic opto bi-stabilization element 42). As a modulation from the primary electric optical effect, it is said to have the response of 10^{-14} sec.

On the other hand, there have been studies of wave guide path on organic crystals 12,43,44). If the wave guidance is possible, in bulk crystalization, constants that are impossible to phase match such as d_{11} , d_{33} can be used by the phase matching method using mode dispersion. If fiber can be formed, a long effective length can be used. There have been some obsevations of SHG on organic crystals by making fibers or plate wave guide paths, but their researches have just started 12,45,46). The problem of the thick film control for the phase matching in wave guide path may be solved by such as two dementional phase matching 47) and layering of monomolecular layer film (LB film). I would like to

note h[illegible]st in the plate wave guide path method using MNA, there is a theoretical calculation which indicates that SHG transformation of 10% efficiency is possible by using a 100mW pump beam 48). As for the LB film, its research which includes tertial nonlinear properties, has just started 49,50).

5. Conclusion

Because the subject here is organic compounds, there are many technical terms in the chemical field which I am not familiar with. The synthsizing of new materials is mostly done by chemists. I strongly felt the necessity of having the cooperation of people in the chemical field.

References

28) Y. Harada:Quntum chemistry (Shokabo.. 1982)